

Evaluation of several commercially available cationic polymer flocculants for phosphate sorption in water.

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Abstract

Although inorganic phosphate is an essential plant nutrient, elevated levels in surface waters may lead to adverse effects in the environment. These effects are attributed to runoff from rain or irrigation events that may cause the sorbed phosphate to be transported from the application sites and move into neighboring watersheds. Increased phosphate concentration in watersheds may lead to a variety of environmental problems including, increased algal blooms, bacterial contamination, and in some cases eutrophication. To overcome these effects, polymer flocculants have been shown to reduce the phosphate concentration in water by removing suspended solids and thereby removing the phosphate sorbed to the solids. The purpose of this study was to determine the amount, if any, of phosphate removed by several commercial polymers. The polymers chosen included the polyacrylamides Magnifloc 494C, Magnifloc 985N and Poly (diallyldimethyl ammonium chloride) (Poly (DADMAC)). Using these polymers it was discovered that the positive charge density of the polymers affected the amount of phosphate removed from solution with Poly (DADMAC) (having 100% positive charge density) removing 40% of the phosphate from a solution containing 10 ppm phosphate.

Keywords

Polymer Flocculants, Phosphate, Sorption, Polyacrylamides, Poly (DADMAC), Smectite

1. Introduction

Phosphorus is an essential plant nutrient that is commonly applied as a fertilizer and is frequently found in surface water. Inorganic phosphate contamination leads to a variety of environmental problems with water resources including increased algal blooms, bacterial contaminations, and eutrophication of surface water bodies as well as rivers and streams [1-5]. The source of phosphate can come from runoff from agricultural fields, land application of wastewater from concentrated animal feeding operations, and municipal wastewater [2; 4; 5]. To help alleviate these adverse effects of phosphate on the environment, methods for the removal of inorganic phosphate from water are needed.

While the removal of phosphate from water is a topic of recent interest, the sorption of phosphate onto polymer flocculants has not been fully investigated [2; 6-11]. Polymer flocculants are routinely used to remove solid material from water [12]. They are added to municipal as well as industrial wastewater to remove suspended solids prior to further treatment to remove dissolved contaminants. These polymer flocculants interact with the surface of suspended solids, organizing the individual particles into larger structures called flocs. The flocs then settle out of solution faster as they have a larger diameter than the individual particles. Polymer flocculants can remove contaminants that are bound or incorporated into the suspended solids through the settling process. Recent work by our team has shown that polymer flocculants can be modified to increase the polymers ability to sequester phosphate from solution [7]. The results from that study showed that the polymer flocculants were able to remove phosphate as well, but at a lower level than the modified polymers that were developed for that study. However, the commercially available polymers did show a trend indicating that increasing the positive charge density of the polymer resulted in increased phosphate removal from solution. It is the effect of positive charge density on the amount of phosphate removed from solution that was the focus of this study.

2. Materials and Methods

The purpose of this study was to evaluate the removal of H_2PO_4^- from water by flocculation using several commercially available polymers. Surface waters have many components including both dissolved and particulate matter. For this study, smectite was chosen to represent the particulate matter present in surface waters as it is a common mineral that has been shown to have slight H_2PO_4^- sorption [13]. Deionized water was used to control the amount of phosphate present, and NaH_2PO_4 (Sigma-Aldrich S8282-550G) was added to create aqueous solutions with different H_2PO_4^- concentrations.

Cationic and nonionic polymers were chosen for this study. The cationic polymers evaluated were polydimethylammonium Chloride (100% positive charge density), Magnifloc 494C (10% positive charge density), and A14 (40% positive charge density). A14 was a polyacrylamide made in-house following the synthesis described in our previous work [7]. Magnifloc 985N was used as a control polymer with no positive charge (Figure 1).

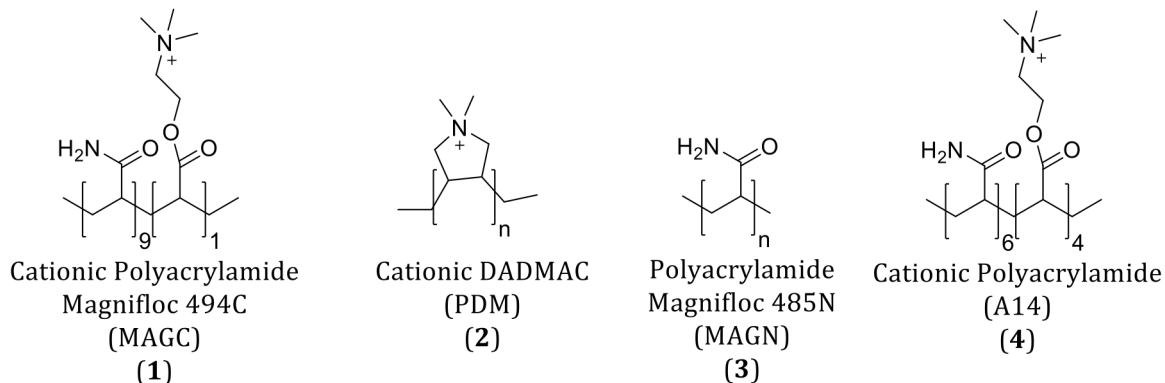


Figure 1. Chemical structures of polymer flocculants.

*Special description of the title. (dispensable)

Three variables were evaluated in this study. First, the amount of smectite was varied to determine the effect on the sequestration of H_2PO_4^- by the polymers. Second, the amount of time the mixture was stirred was varied to determine if there was a kinetic effect on the amount of H_2PO_4^- removed from solution by the polymers. Third and finally, the amount of H_2PO_4^- in solution was varied to determine the sorption maximum.

The following method describes the general experimental procedure with the amounts and concentrations varied as needed for each of the three studies and detailed in Table 1. Smectite was weighed and added to a 25 mL glass Erlenmeyer flask (Kimble KIMAX Flask with ST16 Glass

Stopper, Graduated, 26600). 18.5 mL of deionized water was then added to the flask, which was sealed using a glass stopper. The mixture was then vortexed for 5 s and the resulting mixture was left for 24 hours to allow the smectite to swell and minimize its phosphate sorption. To this mixture 0.5 mL of H_2PO_4^- was added to spike and to obtain the desired H_2PO_4^- concentration. The mixture was then vortexed for 5 s. To this mixture 1 mL of the polymer solution was added to make the final polymer concentration of 100 ppm and a final volume 20 mL. The mixture was then vortexed again for 5 s, a stir bar was added to the flask, and sealed with a glass stopper and then placed on a stir plate (JEIO TECH, Multi channel Stirrer, Model: MS-53M) at 250 RMP for the allotted amount of time.

There were two control experiments that were examined with each of the polymer experiments. The first control was to examine the amount of H_2PO_4^- removed by the smectite. This control was prepared as above but with the addition of 1 mL of water in place of the polymer. The second control contained only H_2PO_4^- , no smectite, and 1 mL of water was added in place of the polymer. After the appropriate amount of time on the stir plate, the stir plate was stopped, the stir bars were removed and 8 mL of solution were placed in a centrifuge tube. The solutions were then centrifuged (Eppendorf Centrifuge 5810) at 3500 RPM for 15 min to remove any solid material that might be present. The supernatant was then filtered through a 0.2 μm syringe filter and analyzed for H_2PO_4^- using a Dionex ICS 2100 ion chromatography system (Suppressor, AERS 500 2 mm, Guard and analytical Column, AG18, AS18) with a 25 μL injection loop, running at a flow rate of 0.25 mL/min in gradient mode (23 mM KOH for 13 min then 30 mM KOH for 12 min) resulting in an elution time for phosphate of 23 min.

3. Results and Discussion

3.1. Effect of Increasing the Amount of Smectite Added

The first experiment conducted was to determine the effect of increasing the amount of smectite added to the mixture. It was assumed that as more smectite was added less of the polymer would be available to interact with the H_2PO_4^- in solution, as it would be adhered to the surface of the smectite particles. The results initially support this assumption as the polyacrylamides generally removed less H_2PO_4^- with additional smec-

Table 1. Experimental Conditions

	Effect of increasing H_2PO_4^-	Effect of Increasing Smectite Added	Effect of Time
H_2PO_4^- (ppm)	1, 5, 10, 15, 25, 30, 50, 60, 75, 100	10	10
Smectite (mg)	150	25, 50, 75, 100, 150, 200, 250, 300, 350, 400, 500	150
Time (Hour)	24	24	0.5, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36

tite added up to 100 mg (Figure 1). The smectite control also showed an increase in H_2PO_4^- adsorption from 4% to 10% at 100 mg. The nonionic polyacrylamide MAGN removed an additional 5% of the H_2PO_4^- from solution above the amount removed by the smectite alone, up to 100 mg of smectite added. The amount of H_2PO_4^- removed by MAGC and A14 generally trended downward with the addition of smectite up to 100 mg with A14 removing the most H_2PO_4^- of all the polyacrylamides at 28%. Generally, the polyacrylamides increased the amount of H_2PO_4^- removed with increased smectite added, up to 35% for A14 at 500 mg of smectite added. PDM diverged from these trends by increasing the amount of H_2PO_4^- removed up to 100 mg of smectite added, followed by a slight decrease in the H_2PO_4^- removed with increasing smectite added.

The results from the polymers up to the 100 mg smectite addition was likely caused by saturation of the negative charge of the clay by the positive charge of the polymer. When there is a high enough concentration of the cationic polymer flocculant compared to the solid material present the charge of the solid material can become negated, thereby changing net charge of the clay-polymer complex [6; 14; 15]. This has the effect of impairing the polymers ability to form flocs and settle out of solution. The net result of this oversaturation of solid material is dispersion as the now neutral or positively charged smectite-polymer complexes repel each other. Given the smallest amount of smectite added (25 mg to 100 mg), less of the polymer was available to interact with H_2PO_4^- in solution so the amount of H_2PO_4^- removed with increasing smectite weight added was observed. The results from additional amounts of smectite above 100 mg up to 500 mg trended toward more H_2PO_4^- removed from solution, however, they were also within error of each other. Given these results, 150 mg of smectite was chosen as the amount of smectite that would be added to the following experiments and remain constant as described in Table 1.

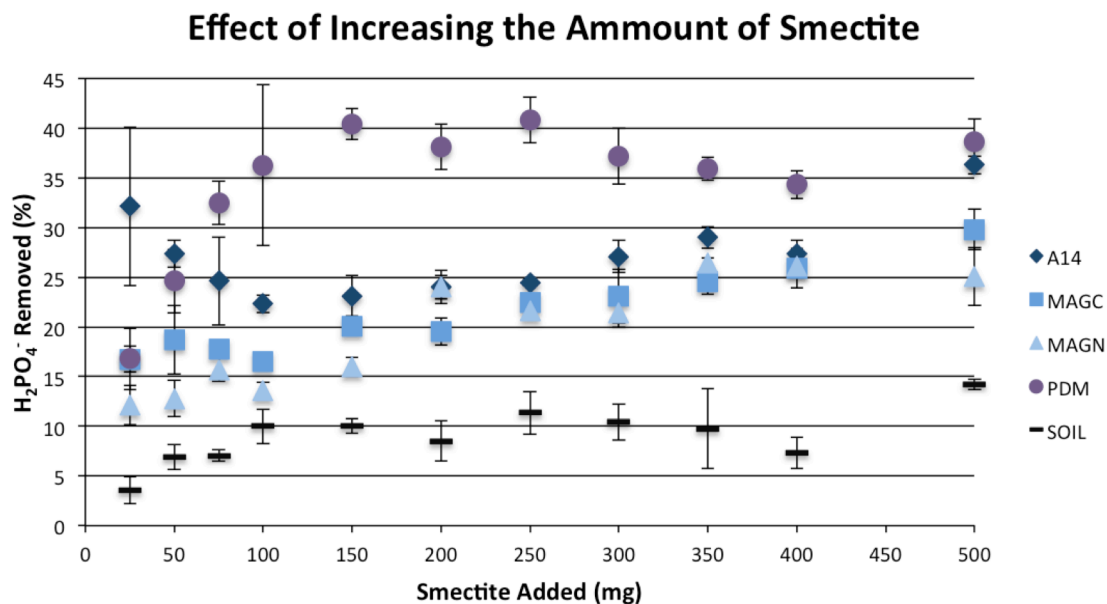


Figure 2. The effect of increasing the amount of smectite added to each flask from 25 mg to 500 mg.

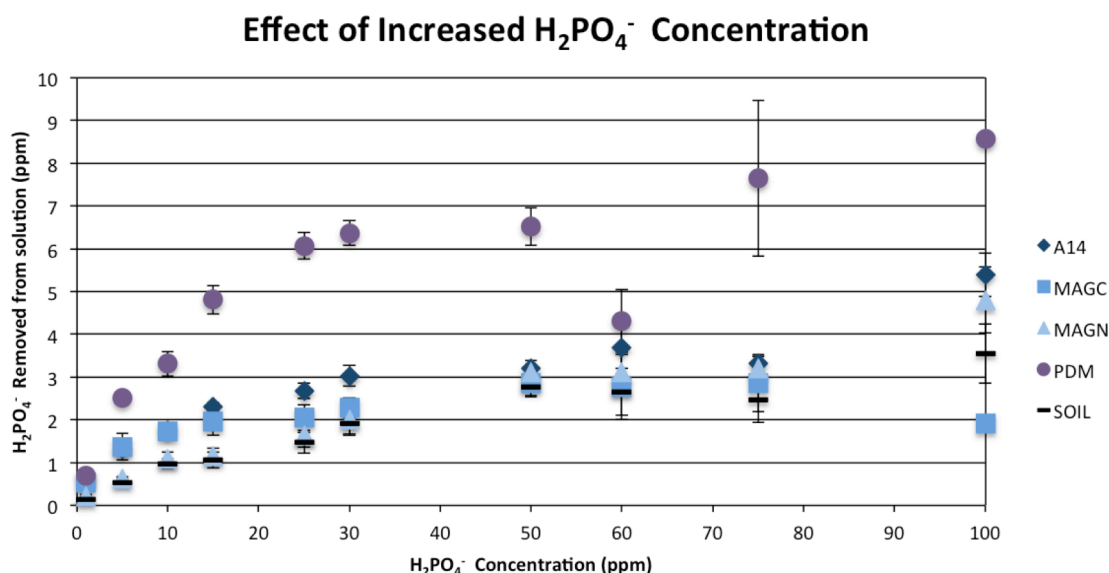


Figure 3. Effect of increasing the solution concentration of H_2PO_4^- from 1 ppm to 100 ppm on the amount of H_2PO_4^- removed from solution.

3.2. Effect of Increasing H_2PO_4^- Concentration

As the solution concentration of H_2PO_4^- increased from 1 ppm to 100 ppm the general trend was an increase in the amount of phosphate removed from solution for all the polymers tested as well as smectite alone. In the H_2PO_4^- concentration range of 1 – 50 ppm, the polymers continued the trend of increasing the amount of H_2PO_4^- removed from solution with increasing positive charge density of the polymer. For the concentration range of 50 – 100 ppm H_2PO_4^- the polyacrylamides removed the same amount of H_2PO_4^- as smectite alone and were within error of each other. PDM with 100% positive charge density consistently removed more H_2PO_4^- from solution than the other polymers tested. At 100 ppm H_2PO_4^- PDM removed almost 9 ppm of H_2PO_4^- , however, the error associated with the PDM results began to increase as the concentrations increased above 50 ppm H_2PO_4^- . From the results of this experiment a concentration of 10 ppm H_2PO_4^- was chosen for use in the next study to observe the effect that the amount of time the polymer mixtures were stirred for would have on the amount of H_2PO_4^- removed from solution.

3.3. Effect of Mixing Time of H_2PO_4^- Sorption.

The third and final study examined the effect of mixing time on the amount of H_2PO_4^- removed from solution. In general, the results again show that an increase in positive charge density of the polymer results in more H_2PO_4^- removed from solution. The smectite control experiment showed an increase in H_2PO_4^- sorption from ~2% to ~7% H_2PO_4^- removed in the first two hours. After this the smectite drifted toward more H_2PO_4^- removed from solution up to ~10% at 36 hours. The nonionic polyacrylamide MAGN effectively followed the results from smectite alone, removing only what the smectite had sorbed. The MAGC and A14 followed similar trends up to 18 hours with A14 removing more H_2PO_4^- from solution than MAGC. After 18 hours, A14 and MAGC generally removed similar amounts of H_2PO_4^- . PDM increased its H_2PO_4^- sorption up to ~35% at 10 hours and maintained that level of sorption, within error out to 36 hours. In all cases, including the smectite control, the amount of H_2PO_4^- removed remained constant after the maximum was reached suggesting an irreversible binding.

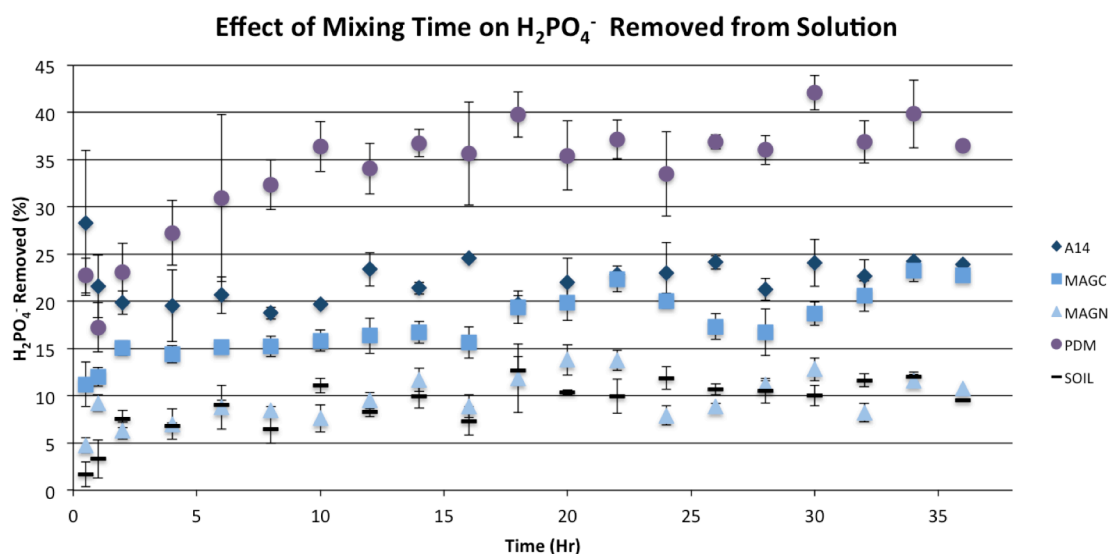


Figure 4. Effect of allowing the mixture to stir for increasing amounts of time on the amount of H_2PO_4^- removed from solution.

4. Conclusions

The results from these studies show that it is possible to remove H_2PO_4^- from solution using cationic polymer flocculants. Generally, an increase in positive charge density will increase the amount of H_2PO_4^- removed from solution. The relationship between the charge density and the amount of H_2PO_4^- removed is not linear, however, with results from A14 with a charge density of 40% at best doubling the amount of H_2PO_4^- removed compared to MAGC with a 10% charge density. The results presented here represent the amount of H_2PO_4^- removed from solution and it is assumed that the H_2PO_4^- sorbed to the polymer was the difference between the H_2PO_4^- removed by the smectite without the addition of polymer and the amount of H_2PO_4^- removed when the polymer and smectite were added. The polymers were not extracted and analyzed separately to determine if the H_2PO_4^- was bound to the polymer or to the smectite. However, the reproducibility of the effect of positive charge density on the amount of H_2PO_4^- removed suggests that the H_2PO_4^- is interacting with the polymers.

The total amount of H_2PO_4^- removed from solution was small (~2 to 4 ppm) considering that phosphate concentrations in Concentrated Animal Feeding Operations CAFO wastewater can be greater than 100 ppm [16]. However, the focus of this study was to evaluate the binding of H_2PO_4^- to the polymers and thus smectite was chosen as it has little H_2PO_4^- sorption. Smectite does have a high negative charge density, however, that might have resulted in more of the polymer interacting with the surface of the clay particle leaving less of the polymer to interact with the H_2PO_4^- in solution. Future work will evaluate changing the charge density of the solid material used in the experiments to determine if it has any effect on the amount of H_2PO_4^- sorbed by the polymers.

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